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Giant Cu 2p Resonances in CuO Valence-Band Photoemission

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We report the observation of a giant resonance in the Cu 2p resonant-photoemission spectra of CuO. The study allows the unambiguous identification of the local Cu $3d^8$ configuration in the valence-band photoemission spectrum, providing conclusive evidence for the charge-transfer nature of the insulating gap in the electronic structure of CuO. A comparison with 3p resonant-photoemission measurements is also presented to emphasize the strength of 2p resonant photoemission as a tool for studying the electronic structure of highly correlated 3d transition-metal systems.

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Resonant photoemission is a well-established technique for studying the electronic structure of solids. It provides a unique means to identify the character of the various states involved in the one-electron removal process. This technique is of particular interest for solids where electron-correlation effects are expected to play an important role in the electronic structure. Numerous resonant-photoemission studies have been carried out using photoenergies close to the 3p absorption edges for 3d transition-metal systems (elements [1], compounds [2] including high-T_c superconductors [3], and impurities [4]). The observed resonance behavior is usually rather weak, and the spin-orbit splitting of the 3p level is relatively small compared to the core-hole lifetime and the energy spread of the various intermediate states in the resonance process, causing the interpretation of the data to be not always straightforward and in some cases nonunique. In the case of CuO, despite the fact that the 3p resonance is one of the strongest in all 3d transition-metal systems and its study is at the basis of the current interpretation of resonant- and nonresonant-photoemission data, it is still possible to envision different models for its electronic structure. Based on a detailed reanalysis of existing photoemission data, it has in fact been suggested [5] that the nature of the insulating correlation gap is Mott-Hubbard rather than charge-transfer-like, as previously conceived [6–10]. Furthermore, that study [5] also proposed to reconsider the mechanism of the 3p resonant-photoemission process, with important implications on the current understanding of the electronic structure of transition-metal compounds including high-T_c superconducting cuprates, for which CuO is generally considered a model system.

We have conducted a new resonant-photoemission study on the electronic structure of CuO using photon energies in the vicinity of the Cu 2p absorption edges. This was done in order to demonstrate the advantage of 2p as compared to 3p resonant photoemission as a tool for probing the electronic structure of 3d transition-metal systems. This in turn will enable us to appraise the different views on the electronic structure of CuO and in particular on the nature of the insulating gap. We observed a giant-resonance behavior with intensities 2 orders of magnitude larger than the direct photoemission and 3p resonant-photoemission signals. These 2p giant resonances conclusively identify the energy positions of the local Cu $3d^8$ character in the one-electron removal spectrum, and consequently demonstrate that CuO is a charge-transfer insulator.

These measurements were performed using the AT&T Bell Laboratories Dragon high-performance soft-x-ray beam line [11] at the National Synchrotron Light Source. The electrons were collected with a Vacuum Science Workshop HA-150 hemispherical analyzer equipped with multichannel detection. To facilitate the direct comparison of the spectra, the overall monochromator and analyzer resolution was set at a value close to the 2p core-hole lifetime, ~ 1 eV, for all photon energies below, at, and above the Cu $2p_{3/2}$ white line. High-resolution spectra have also been taken at the white line to assess the effect of instrumental resolution, and the spectra were found to be essentially the same. The CuO sample was prepared *in situ* by high-pressure (1–10 torr O_2) and high-temperature (400 °C) oxidation of polycrystalline Cu as described in an earlier study [6], yielding Cu 2p and O 1s levels and valence-band x-ray photoemission spectra identical to those measured previously.

Figure 1(a) shows the valence-band photoemission spectra with photon energies in the vicinity of the Cu $2p_{3/2}$ absorption edge, while in Fig. 1(b) the same spectra are expanded by a factor of 10. The inset to Fig. 1(a) depicts the $2p_{3/2}$ absorption spectrum with the white line at 931.3 eV. The vertical lines and corresponding numbers indicate the selected photon energies for the photoemission spectra. The off-resonant photoemission spectrum (curve 0) was taken at a photon energy 12 eV below the white line, showing a main peak at a binding energy around 2–6 eV and a satellite peak around 8–16 eV. Going towards the white line (curves 1 to 7), the satellite intensity increases, reaching its maximum at the white line

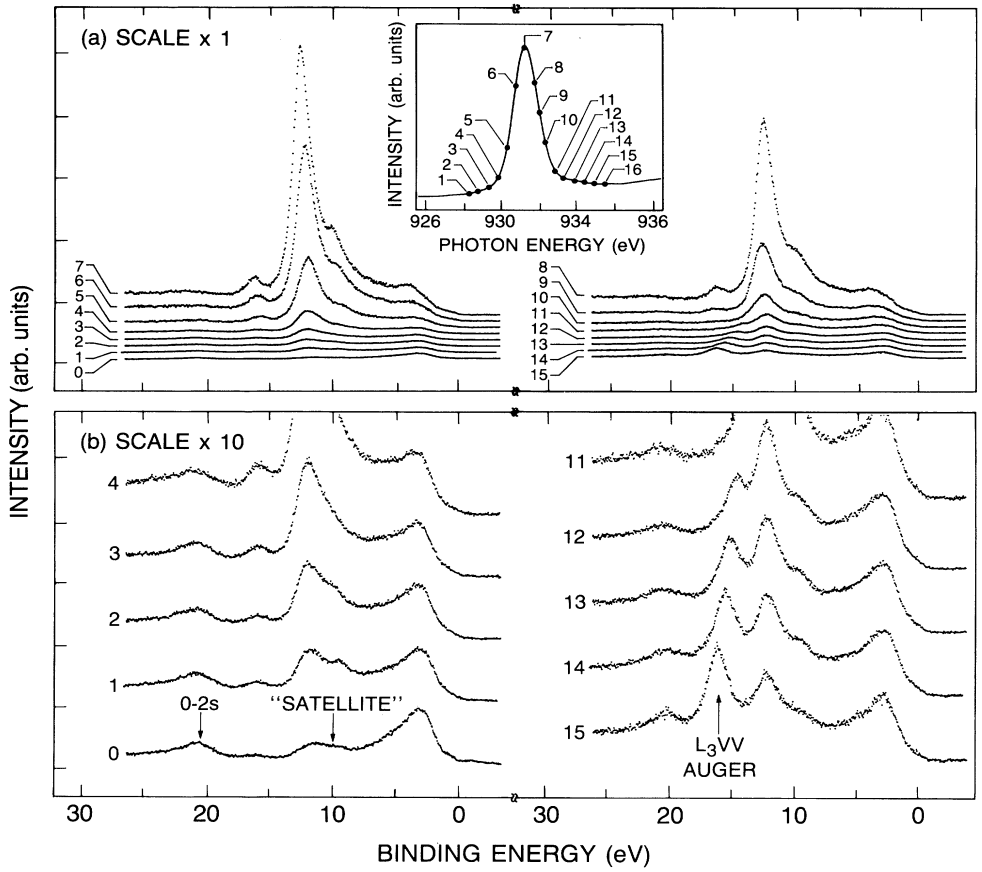

FIG. 1. (a) Valence-band photoemission spectra of CuO recorded using photon energies near the Cu $2p_{3/2}$ edge. The labels of the spectra correspond to photon energies indicated by the dots in the inset which shows the Cu $2p_{3/2}$ photoabsorption spectrum with the white line at 931.3 eV. The spectrum labeled 0 is taken at 12 eV below the white line. These spectra are normalized to the photon intensity. (b) The same spectra but with the vertical scale expanded by a factor of 10.

(curve 7), and then decreases at higher photon energies (curves 8 to 15). For energies several eV above the white line (curves 11 to 15), the regular L_3VV Auger signal appears and the off-resonance photoemission is recovered. The photoemission intensity at the resonance maximum is 30 times larger than the regular L_3VV Auger and 100 times larger than the off-resonant photoemission. The resonant behavior is predominantly affecting the satellite states. The identification of the electronic configuration corresponding to these states and, consequently, to those of the main peak constitutes the object of the subsequent discussion and is fundamental for the comprehension of the nature of the insulating gap.

It is generally accepted that electron-correlation effects play an important role in the electronic structure of CuO [10]. For instance, a band-structure calculation (one-electron theory) cannot explain the large satellite structure observed in direct valence-band photoemission spectra [6,7]. Cluster or impurity model calculations which include configuration interaction and atomic multiplet theory on the other hand give a good agreement [7, 12–15]. It is found that the valence states are dominated by the d^8 and $d^9\underline{L}$ configurations, where $\underline{L}$ denotes an O $2p$ ligand hole, and that the d^8 final states are higher in energy than the $d^9\underline{L}$ states. In these calculations the on-site Cu $3d$ Coulomb interaction U_d is deduced to be ~ 8 eV, a value larger than the Cu $3d$ to O $2p$ ligand charge-transfer energy Δ (~ 3 eV), and therefore the insulating gap is classified to be of charge-transfer nature [6,7,10].

This picture is strongly supported by the resonant-photoemission data. The current understanding [16] of this resonant process is that two different photoemission channels are present when the photon energy is near the Cu np ($n=2,3$) absorption edge. These two channels are the direct photoemission channel ($3d^9+h\nu \rightarrow 3d^8+e$) and the deexcitation channel, a photoabsorption process followed by a super Coster-Kronig Auger decay ($np^6 3d^9+h\nu \rightarrow np^5 3d^{10} \rightarrow np^6 3d^8+e$). The deexcitation channel probes only the d^8 final states and, due to the identical initial and final states of these two channels, the interference effect leads to Fano-type [17] resonance or antiresonance behavior for states with d^8 character.

In the $2p$ resonant-photoemission case, the giant-resonance behavior observed demonstrates that the deexcitation channel overwhelms the direct photoemission channel. The resonance therefore directly reflects the d^8 final states and the data clearly show that the d^8-like satellite states are on the high-binding-energy side of the $d^9\underline{L}$-like main peak, in agreement with the charge-transfer picture. Moreover, the line shape of the resonant spectrum (curve 7) is very similar to the regular Auger spectrum [18] and to the Cu $2p_{3/2}$ Auger-photoelectron-coincident spectrum [19] of Cu metal, for which the dominant Auger process is a $2p^5 3d^{10} \rightarrow 2p^6 3d^8 + e$ transition, giving evidence that the resonance spectrum indeed derives from the d^8 final states. The peaks at 12.5- and 16.2-eV binding energy contain the typical atomic ^1G and ^1S characters, respectively. Further experimental evidence to the above-mentioned analysis is given by the analogous, but much weaker resonance behavior observed in previous Cu $3p$ resonant-photoemission measurements [2,8,9], which require a more careful analysis [8,20] because interference effects leading to Fano-type resonances are important.

A recent study [5] based on a critical reanalysis of existing photoemission data and the use of an alternative theoretical model, which includes, for example, the hybridization between O $2p$ and Cu $4s$ bands, however, has provided an alternative view on the nature of the insulating gap of CuO. In this study, U_d ($\sim$6 eV) is found to be smaller than Δ ($\sim$8 eV) and, consequently, the d^8 states are lower in binding energy than the $d^9\underline{L}$ states and the insulating gap is more Mott-Hubbard-like. This is in obvious contrast with the results of the $2p$ resonant-photoemission measurements, where the resonating d^8 states are higher in energy than the $d^9\underline{L}$ states. In the case of the $3p$ resonant-photoemission data, this discrepancy was tentatively associated with a possible role of the low kinetic energy ($\sim$70 eV) of the escaping electron, which might lead to an adiabatic rearrangement of the core potential thereby enhancing the $d^9\underline{L}$-like satellite at the expense of the d^8-like main peak in the resonance process (assignment within the Mott-Hubbard picture). However, this adiabatic effect, if any, is insignificant at the $2p$ edge, because the electron kinetic energies are as high as 900 eV and, therefore, the higher-lying satellite showing the largest resonance behavior is necessarily of d^8 character (assignments within the charge-transfer picture).

To further confirm the charge-transfer insulator nature of CuO, Fig. 2 compares the experimental data to a $2p$ resonant-cluster-photoemission calculation which includes both the direct photoemission and deexcitation channels. The parameters used in this calculation are identical to those used in a previous $3p$ calculation [8] except for core-level-dependent atomic photoabsorption and Auger matrix elements [21]. The calculation is in good agreement with the experiment (some discrepancies in the peak positions are due to the limited number of O $2p$ orbitals included in the cluster). A breakdown of the calculated spectrum into singlet and triplet parts shows that the singlet (particularly the one which is ^1G-like) resonates more strongly than the triplet as expected, because the Auger matrix elements for the atomic ^1G states are by far the largest in the L_3VV Auger spectra of Cu metal [18].

Although the major intensity increase in the spectra occurs between 8- and 16-eV binding energy, due to the strong hybridization between d^8 and $d^9\underline{L}$ states, the resonant effects are observed, to a lesser degree, across the whole spectrum. An enlargement of the on- and off-resonant spectra near the Fermi level is shown in Fig. 3. The difference of these two spectra, an estimate for the

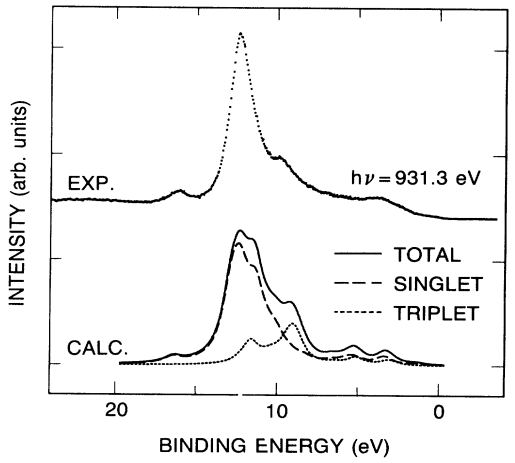

FIG. 2. Comparison between calculated and measured Cu $2p_{3/2}$ on-resonance valence-band photoemission spectra. The dashed, dotted, and solid lines are the calculated singlet, triplet, and total spectrum, respectively. A Lorentzian broadening of 1.2 eV is included in the cluster calculation.

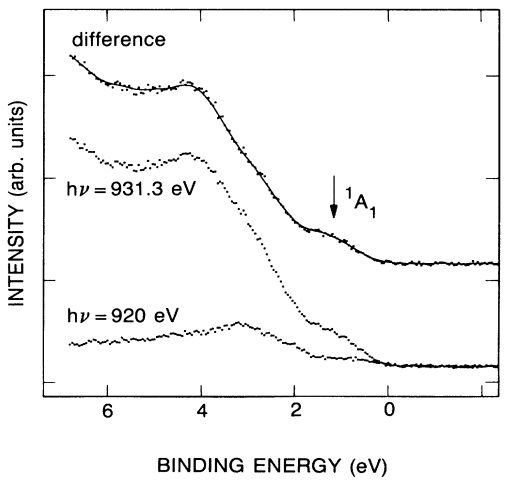

FIG. 3 Valence-band photoemission spectra of CuO near the Fermi level. The on-resonance ($h\nu$=931.3 eV), off-resonance ($h\nu$=920 eV), and difference spectra are normalized to the photon intensity.

pure d^8 character, clearly shows that this character is present at the energy of the first ionization state. In fact, in order for the first ionization state to become a singlet [7,12,14,22] (identified as $^1A_1$ in a square planar CuO_4 cluster), it requires some admixture (~7%, Ref. [7]) of the d^8 character into the primarily $d^9\underline{L}$-like state. Interestingly, this state shows strong $2p$ resonance yet weak $3p$ antiresonance [8,9]. The strong resonance observed for this state motivates the use of angle-dependent $2p$ resonant-photoemission measurements to probe the low-lying local singlet and triplet states in high-T_c superconductors.

In conclusion, the giant resonances observed in this work, showing that the d^8 states are higher in binding energy than the $d^9\underline{L}$ states, provide conclusive evidence for the charge-transfer nature of the CuO insulating gap and resolve the current debate on the electronic structure of this oxide. The strong resonant enhancement together with the large $2p$ spin-orbit splitting that simplifies the analysis of the spectra, and the rich structure typically observed in the $2p$ photoabsorption spectra of transition-metal systems [23], offers a unique opportunity to map out various characters in the one-electron-removal spectra by selecting different intermediate states for the deexcitation channel. These intermediate states could result from atomic multiplet splitting, ligand-field effect, or configuration interaction.

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